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D. D. Elleman and

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**NMR DOUBLE RESONANCE TECHNIQUES FOR THE
DETERMINATION OF RELATIVE SIGNS OF
SPIN SPIN COUPLING CONSTANTS**

D. D. ELLEMAN and S. L. MANATT

*Physical Sciences Division, Jet Propulsion Laboratory,
California Institute of Technology, Pasadena, California*

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Double irradiation of high resolution NMR spectra makes it possible to determine the relative signs of some or all of the spin spin coupling constants. The technique has been used to determine the relative signs of not only proton proton coupling constants but also fluorine proton and fluorine fluorine coupling constants.

AUTHOR

La double irradiation de spectres de résonance magnétique nucléaire à haute résolution permet de déterminer les signes relatifs de quelques-unes ou de toutes les constantes de couplage spin-spin. La technique a été appliquée pour déterminer non seulement les signes relatifs des constantes de couplage entre protons mais aussi des constantes de couplage entre noyaux de fluor et protons et entre noyaux de fluor.

Recent theoretical work by Karplus^{1, 2)} has stimulated interest in the determination of relative and absolute signs of spin-spin coupling constants. In theory it is possible to experimentally^{3, 4, 5)} determine the relative signs of proton coupling constants by diagonalizing the Hamiltonian, obtaining the allowed transitions, and then comparing these transitions with the experimental spectra. In this case there must be at least three groups of chemically shifted nuclei and all nuclei must be coupled with one another⁶⁾. The decision as to the relative signs of the coupling constants depends on the observation of small shifts in positions of the transitions and small intensity changes which are in general at the limits of experimental detection. It is often necessary to obtain spectra at two frequencies and compare the assignments of relative signs at these two frequencies⁷⁾. Also, observation of proton spectra at very low magnetic fields where the protons are strongly coupled has been used⁸⁾. In general, high resolution analysis of weakly coupled spin systems does not give any information of relative-sign assignments. The determination of relative signs of coupling constants has been greatly hindered by the above mentioned difficulties.

Recently double irradiation techniques have been used by several laboratories to determine relative signs of proton spin-spin coupling constants^{9, 10)}. This technique alleviates the tedious measurement of spectra

and the cumbersome numerical calculation of high resolution techniques. The double irradiation of proton-proton systems has been performed by the audio side band phase detection method which is described in detail elsewhere¹⁰). In this paper we extend this technique to the determination of the relative signs of fluorine-fluorine coupling constants and fluorine proton coupling constants.

The first step in applying the double irradiation technique for sign determination is to label each transition of the spectrum according to its origin in the limit as all the ratios J_{ij}/δ_{ij} approach zero (J_{ij} is the coupling constant between nuclei i and j ; δ_{ij} is the chemical shift between nuclei i and j) and then to write down for each transition a table of the spin states of all the neighboring nuclei which are coupled to the nucleus responsible for that particular transition.

TABLE I
Spin states of neighboring nuclei for coupling constants all of the same relative sign

Origin	A				B				C			
Transitions	1	2	3	4	5	6	7	8	9	10	11	12
Spin states												
A					α	β	α	β	α	β	α	β
B	α	α	β	β					α	α	β	β
C	α	β	α	β	α	α	β	β				

Fig. 1 (a) shows the normal high resolution fluorine spectrum of tri-fluorobromoethylene recorded at 56.4 Mc/sec. Transitions 1 through 4 are assigned to the A fluorine nucleus; transitions 5 through 8 to the B nucleus, and transitions 9 through 12 to the C nucleus. It is noted that the chemical shift, δ_{ij} 's, between the various groups of lines is large compared to the coupling constants J_{ij} 's; therefore, usual high resolution calculations do not give any information on the relative signs of the coupling constants in this case. Table 1 shows the spin states of the neighboring nuclei for each transition and is constructed with the assumption that all of the signs of the

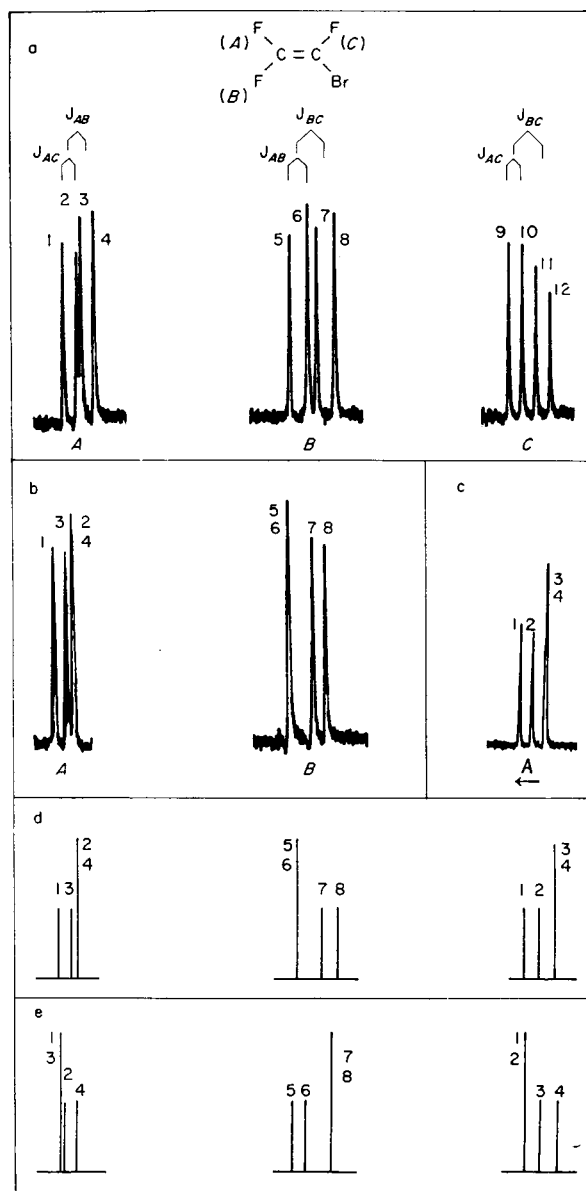


Fig. 1. F^{19} NMR spectrum of 1,1,2-trifluoro-3-bromoethylene: *a*, phase detected undecoupled; *b*, A region when lines 5 and 6 irradiated and B region when lines 2 and 4 irradiated, $\gamma H_1/2\pi = 150$ cps; *c*, A region when lines 9 and 10 of C region irradiated, $\frac{1}{2}H_1 = 150$ cps; *d*, changes predicted on double irradiation as described in *b* and *c* above if J_{AC} and J_{BC} of different sign and J_{AB} and J_{BC} of different sign (far right); *e*, changes predicted in *b* and *c* if all the signs are the same.

coupling constants are the same. The notation employed in the table is that an α state corresponds to $m_i = +\frac{1}{2}$ and a β state corresponds to $m_i = -\frac{1}{2}$.

It is well known that if lines 1 through 4 are irradiated with a large R. F. field [$\gamma H_1/2\pi \gg J_{ij}$ or $H_1 = 80$ milligauss] and simultaneously the B region of the spectrum is observed in the usual manner, lines 5 and 6 collapse to a single line and lines 7 and 8 also collapse to a single line. Thus, one observes a doublet in the B region of the spectrum and the doublet has the spacing equal to J_{BC} .

If transitions 1 and 3 are strongly irradiated without irradiating transitions 2 and 4 it is seen from the table that only those transitions which have the C nucleus in the α state are being irradiated while the transitions which have the C nucleus in the β state are not being strongly irradiated. Thus, transitions 5 and 6, the transitions that have the C nucleus in the α state, should collapse, and transitions 7 and 8 should not be affected. To perform this experiment the R. F. field H_1 is reduced such that $\gamma H_1/2\pi \cong J_{ij}$ and the strong irradiation is applied between transitions 1 and 3. Transitions 5 and 6 should collapse if the sign of the coupling constants J_{AC} and J_{BC} are the same. If the sign of the coupling constants are different from one another, then the α 's and β 's in row C column's B must be interchanged. It is then seen that lines 7 and 8 should collapse when lines 1 and 3 are irradiated. In a similar manner, it can be shown that when lines 2 and 4 are strongly irradiated lines 7 and 8 should collapse if the signs are the same and 5 and 6 should collapse if the signs are different.

Fig 1 (b) and 1 (c) show the experimental data from a set of double irradiation experiments. Fig. 1 (d) and 1 (e) show the predicted spectra for various relative sign assignments. It is quite obvious that J_{AC} and J_{BC} have different signs and J_{AB} and J_{BC} have different signs. Thus, J_{AB} and J_{AC} have the same sign.

A similar set of experiments have been performed on the molecule trifluoroethylene. For this molecule, the fluorine-fluorine relative signs are the same as for the trifluorobromoethylene described above. In addition, J_{AH} and J_{BH} were found to have a different relative sign and J_{BH} and J_{CH} were found to also have a different relative sign.

Additional double resonance experiments have been performed on other molecules and the results are given elsewhere ¹¹).

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